Investigating the Catalytic Properties of Hydroxyapatite Derived From Mussel Shells for the Treatment of Wastewater

By

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ABSTRACT

The seafood processing industry in New Zealand and worldwide generates a large amount of shell waste and currently the shell waste under-utilized. The possibility of producing a useful product from this shell wastes will greatly enhance and ensure sustainable economic development as well as the associated waste management problems. Therefore, as one possible solution, the overall objective of this study was to investigate the feasibility of mussel shells waste for the synthesis of hydroxyapatite, $Ca_{10}(PO4)_6(OH)_2$ (denoted as HAP) and other derivatives from mussel shells to act as photocatalyst in degradation of methylene blue and dehydroabietic acid in aqueous media via photocatalysis.

In this study, a novel pyrolysis-wet slurry precipitation process from *Perna Canaliculus* (green-lipped mussel) shells without pH and temperature control has been developed. The process of HAP synthesis involved crushing, calcination of shells into calcium oxide followed by a slurry wet precipitation method, where an aging time of five hours under nitrogen atmosphere was applied. Three different types of HAPs were produced in this study (As-HAP800, calcined at 800 °C, no post heat treatment; As-HAP900, calcined at 900 °C, no post heat treatment; Ht-HAP, calcined at 900°C, post heat treatment at 900 °C) and were compared to a commercial HAP from Sulzer Metco (Com-HAP). HAP with purity comparable to the commercial sample were obtained, as confirmed by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Electron Dispersive X-ray Analysis (EDS) and Inductive Couple Mass Spectroscopy (ICP-MS). The results showed that the as-synthesised HAPs (As-HAP800 and As-HAP900) contained calcium carbonate (calcite) impurity which was mainly caused by incomplete calcination of the mussel shells. This impurity can be removed or reduced by the subsequent heat treatment of the HAP.

The HAP synthesised in this work was used as a photocatalyst, testing two model wastewaters containing methylene blue and dehydroabietic acid respectively in a batch reactor. The effects of different HAP material properties (surface area, band gap energy and the existence of calcite impurities resulting from different calcination temperatures) on the photocatalytic activity and reaction mechanism were investigated for these model wastewaters. The methylene blue degradation pathway was found to be the same as that reported for other semiconductor photocatalysts, indicating that photocatalysis is most likely occurring with the HAP. Among the different forms of HAP studied, As-HAP800 showed the highest overall reaction rate (per unit mass of catalyst) followed by As-HAP900, Com-HAP and Ht-HAP. It was also found that

the degradation rates for reaction at UV irradiation of 254 nm showed higher overall reaction rates per unit mass of catalyst compared to the UV irradiation at 340 nm, which is likely due to the higher energy associated with the 254 nm UV irradiation. The kinetics for the reactions using As-HAP800 and As-HAP900 were well described by three first order reactions in series while Com-HAP and Ht-HAP followed a two-step series of first order kinetics.

To determine the effect of residual unconverted raw materials in the HAP photocatalysts, the photocatalytic degradation of methylene blue using other calcium compounds derived from mussel shells was investigated. Raw shell powder (RS) and calcite (CS540: Calcined mussel shell powder at T=540 ^{o}C) were found to be able to degrade methylene blue but at a lower degradation rate compared to the HAP. The overall degradation rate showed by CaO (CS900: Calcined mussel shell powder at T=900 ^{o}C) was two orders of magnitude higher than those obtained using RS and CS540. However, it was found that the reaction with CS900 was not due to a photocatalytic reaction, but was caused by an oxidation reaction that was highly accelerated in the alkaline conditions during the dark period.

For the photocatalytic degradation of dehydroabitic acid, three reaction intermediates were identified which were 7-hydroxy-dehydroabietic acid, abietic acid and pimaric acid. The kinetics for the reactions were found to fit a pseudo-first-order reaction rate for both batch and annular reactors for all the HAP. A comparison of batch and annular reactors for the degradation of dehydroabietic acid showed that the overall reaction rates and photonic efficiency for the annular reactor was an order magnitude larger than the batch reactor which indicates that the annular reactor was more efficient at utilizing the UV light. However, there were no apparent differences in the mechanism of degradation. It was also found that in annular reactor, higher flow rate resulted in a higher reaction rate. Through this study, it was also found that the stability of the as-synthesised HAP was low which was due to to the dissolution of the HAP especially in the reaction with methylene blue. Therefore, the study on increasing the stability of HAP to act as a good photocatalyst was one of the recommendations to be included in the future work.

Overall, it has been demonstrated that the new process of producing HAP used in this study therefore unlocks a route for recovering and recycling waste shells into HAP and other calcium compounds and its further application for environmental remediation – a potentially 'green' photocatalytic process.

DEDICATIONS

TO:

MY HUSBAND, KHAIRULANUAR ABDULLAH, MY CHILDREN,
IRFAN, ADAM & AMIR
AND
MY PARENTS, SHARIFFUDDIN ABD. KAHAR & YUNIAR
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NOMENCLATURE

ρ	Density of liquid ($kg.m^{-3}$)
μ	Viscosity of liquid ($kg.m^{-1}s^{-1}$)
λ	Light Wavelength (nm)
C	Concentration ($mol.m^{-3}$)
C_0	Initial concentration ($mol.m^{-3}$)
C_{INAR}	Concentration of reactant entering the annular reactor ($mol.m^{-3}$)
C_{OUTAR}	Concentration of reactant leaving the annular reactor ($mol.m^{-3}$)
d	Length of the magnetic bar (m)
E_g	Band gap energy (eV)
h	Planks Constant (J.s)
K	Langmuir adsorption constant ($m^3.mol^{-1}$)
k_{app}	Apparent Reaction Rate Constant on Volume Basis (s^{-1})
k'_{app}	Apparent Reaction Rate Constant on Mass Basis ($m^3g^{-1}s^{-1}$)
k''_{app}	Apparent Reaction Rate Constant on Area Basis ($m^3m^{-2}s^{-1}$)
Q	Volumetric flow rate ($m^3.s^{-1}$)
$(-r_A)$	Rate of reaction per unit volume of solution ($mol.g^{-1}s^{-1}$)
$(-r_{A'})$	Rate of reaction per unit mass of catalyst ($mol.g^{-1}s^{-1}$)
$(-r_{A''})$	Rate of reaction per unit surface of catalyst ($mol.m^{-2}s^{-1}$)
t	Time (s)
u	Velocity of the fluid flow through the reactor ($m.s^{-1}$)
V	Volume of reactor (m^3)
z	Path length of substance (m)

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